The apparent inertness suggests a possible relationship to the steroids of the adrenal cortex [Mason, Myers and Kendall, *J. Biol. Chem.*, **116,** 267 (1936); Reichstein, *Helv. Chim. Acta*, **19,** 1107 (1936)] but so far no additional evidence in support of this attractive hypothesis has been obtained.

The substance was isolated from the neutral total ketonic fraction as the semicarbazone which is strikingly characterized by its practically complete insolubility in boiling organic solvents and water. For analysis the semicarbazone was freed from as many impurities as possible by repeated extractions with hot water, alcohol and acetone. The melting point varied from 300 to 315° (decomp.) with the rate of heating. On hydrolysis with dilute alcoholic sulfuric acid, 103.6 mg. gave 86.0 mg. of the crude ketone; the theoretical yield from a monosemicarbazone of $C_{19}H_{26}O_3$ is 87.1 mg. The product was readily soluble in cold acetone, benzene and chloroform, moderately so in ether and alcohol. The analytical sample was recrystallized four times from alcohol and twice from aqueous acetone. It separated in long white needles melting at 252° (uncorrected) with preliminary softening 3° below this. Nitrogen, halogen and sulfur were absent. *Anal.* (Schoeller) Semicarbazone: calcd. for $C_{20}H_{29}O_3N_3$: C, 66.85; H, 8.08; N, 11.69. Found: C, 67.05, 67.02; H, 7.75, 7.82; N, 10.85, 10.74. Free ketone: calcd. for $C_{19}H_{26}O_3$: C, 75.50; H, 8.61. Found: C, 75.47, 75.50; H, 8.52, 8.45.

The investigation is being continued. Complete experimental details will be published at a later date.

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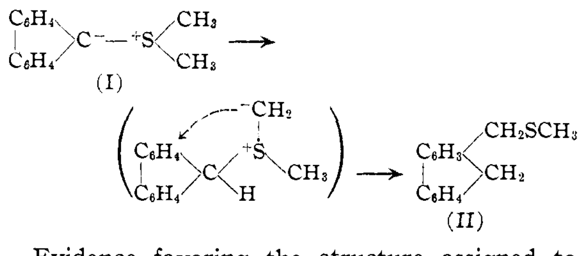
RECEIVED JANUARY 18, 1938

REARRANGEMENT OF FLUORYLIDENE DIMETHYL SULFIDE TO FLUORENE-1-DIMETHYL SULFIDE

Sir:

Recent developments [Sommelet, *Compt. rend.*, **205,** 56 (1937); Krollpfeiffer and Schneider, *Ann.*, **530,** 38 (1937)] along lines closely related to those on which we are working have prompted us to record observations dealing with fluorylidene dimethyl sulfide. Our experiments have revealed that fluorylidene dimethyl sulfide (I), which was discovered by Ingold and Jessop [*J. Chem. Soc.*, 713 (1930); see also Hughes and Kuriyan, *ibid.*, 1609 (1935)], rearranges in an alkaline medium such as alcoholic sodium hydroxide or liquid ammonia to fluorene-1-dimethyl sulfide (II).



Evidence favoring the structure assigned to (II) was secured by graded oxidation. By means of hydrogen peroxide (II) is converted to fluorene-1-dimethyl sulfone, whereas with a stronger oxidizing agent such as sodium dichromate in acetic acid, fluorenone-1-dimethyl sulfone and fluorenone-1-carboxylic acid are formed. The last mentioned compound was characterized by comparison with fluorenone-1-carboxylic acid prepared by the oxidation of fluoranthene. As is to be expected, (II) is converted by methyl alcoholic hydrochloric acid to fluorene-1-dimethyl ether and by a solution of hydrogen bromide in acetic acid to fluorene-1-methyl bromide, which with zinc and acetic acid is reduced to 1-methylfluorene.

BUREAU OF CHEMISTRY AND SOILS GUIDO E. HILBERT
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RECEIVED NOVEMBER 17, 1937

INTERNAL FREE ROTATION IN HYDROCARBONS

Sir:

In a recent note Kassel[1] puts forward certain arguments which imply that free internal rotation occurs in saturated hydrocarbon molecules at room temperatures. Since we cannot agree with several of the points which he has put forward, we should like to discuss them here and at the same time present a very brief summary of the arguments on the other side of this vexatious question.

Kassel bases his reasoning on a comparison for the reaction *n*-butane ⟷ iso-butane of the entropy change obtained from equilibrium and combustion data (−2.1 e. u.) with that from Third Law measurements by Parks, Shomate, Kennedy and Crawford[2] (−5.8 e. u.). He argues that

(1) Kassel, THIS JOURNAL, **59,** 2745 (1937).

(2) Parks, Shomate, Kennedy and Crawford, *J. Chem. Phys.*, **5,** 359 (1937).

"modern determinations of this sort (*i. e.*, of entropy from the Third Law) can only be wrong by failure to attain equilibrium in the crystal and hence can only be too low." With this we disagree because the heat capacities of the compounds in question have been measured only down to 67°K., the extrapolated contribution to the entropy of butane being 9.9 e. u. This extrapolation may be in error in either direction. Indeed, comparing the entropies of saturated hydrocarbons, one finds that the value for butane appears to be high judging by the trend for the others.

Kassel's citation of entropies calculated by Pitzer[3] with inclusion of hindered rotation is really irrelevant because of the arbitrary way in which Pitzer selected the magnitude of the internal restraining potentials. With the now prevalent uncertainty concerning the origin of the restraining potentials it seems doubtful whether any reliable estimates of these potentials can be made in the absence of experimental data. Thus in ethane the restricting potential appears to be 3100 cal./mole,[4] whereas if the entire energy difference of *cis*- and *trans*-butenes-2[5] is assigned to hydrogen interactions much smaller potential barriers for the rotation of methyl groups are indicated. This is cited here merely to show that without the knowledge of the laws of force responsible for the hindrance of internal rotation, entropy calculations for other hydrocarbons than ethane are rather meaningless, except as a method of evaluating the potentials by comparison with experimental entropies. We are not at all certain that Pitzer's calculations are useful for this purpose because of the uncertainty involved in the method of calculation.

In evaluating evidence for and against free rotation there are a number of facts which undoubtedly are more decisive than those Kassel considers: namely, that the entropies of four compounds (C_2H_6,[6] $C(CH_3)_4$,[7] CH_3OH,[8] CH_3NH_2[9]) whose heat capacities have been measured to such low temperatures that the extrapolations do not involve significant accidental errors, are all lower than calculated on the basis of free rotation; that in two instances ($C_2H_6 = C_2H_4 + H_2$,[10] $CO + 2H_2 = CH_3OH$[11]) thermal equilibrium measurements agree much better with these Third Law entropies than with the statistical entropies with free rotation; that the infra-red spectrum of ethane needs the assumption of hindered rotation for a satisfactory explanation[12] and finally that the heat capacity of gaseous ethane at low temperatures agrees better with a hindered rotation model than with one having free rotation.[13]

In view of all this we believe that although the question cannot perhaps be regarded as entirely settled, the preponderant weight of evidence is for the assumption of strongly hindered rotation in these molecules.

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RECEIVED JANUARY 7, 1938

(3) Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).
(4) Kemp and Pitzer, THIS JOURNAL, **59**, 276 (1937).
(5) Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 876 (1935).
(6) Witt and Kemp, *ibid.*, **59**, 273 (1937).
(7) Aston, Siller and Messerly, *ibid.*, **59**, 1750 (1937).
(8) Ahlberg, Blanchard and Lundberg, *J. Chem. Phys.*, **5**, 539 (1937).
(9) Aston, Siller and Messerly, THIS JOURNAL, **59**, 1743 (1937).
(10) Smith and Vaughan, *J. Chem. Phys.*, **3**, 341 (1935); Teller and Topley, *J. Chem. Soc.*, 885 (1935).
(11) Kassel, *J. Chem. Phys.*, **4**, 493 (1936).
(12) Howard, *ibid.*, **5**, 451 (1937). But see Bartholomé and Karwill, *Naturwiss.*, **25**, 476 (1937).
(13) Kistiakowsky and Nazmi, *J. Chem. Phys.* (1938).